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*Experimental and Theoretical Studies of
Intermolecular and Intramolecular Processes*

FINAL REPORT

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The following papers were published or submitted for publication:

1. Large Amplitude Vibrational Motion in a One Dimensional Chain; - Coherent State Representation; With John Dancz. J. Chem. Phys. 67, 1418 (1977).
2. Spectroscopic Properties of Polyenes III: 1, 3, 5, 7-Octatetraene. With R. M. Gavin, Jr., Charles Weisman, Jeffrey K. McVey. J. Chem. Phys. 68, 522 (1978).
3. On Vibrational Population Relaxation in Solution; With Joseph N. Kushick. Chem. Phys. Letters 52, 208 (1977).
4. Internal Energy Transfer in Isolated Molecules: Ergodic and Nonergodic Behavior. In Proceedings of a Symposium on Advances in Laser Chemistry; California Institute of Technology, March, 1978. Ed. A. Zewail. Springer Verlag (1978).
5. On the Influence of Nonrandom Sequential Coupling on Radiationless Relaxation Processes. With M. Muthukumar. J. Chem. Phys. 69, 1619 (1978).
6. On Rotational Effects in Radiationless Processes in Polyatomic Molecules; With Frank Novak and Karl Freed. In Radiationless Transitions, ed. S. H. Lin, (Academic Press). (In press).
7. Single Vibronic Level Fluorescence From Aniline. With Donald A. Chernoff. J. Chem. Phys. 70, 2511 (1979).



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8. Collision Induced Intramolecular Vibrational Energy Transfer in 1B_2 Aniline; With Donald A. Chernoff. J. Chem. Phys. 70, 2521 (1979).
9. A Numerical Study of Large Amplitude Motion on a Chain of Coupled Nonlinear Oscillators; With Timothy J. Rolfe and John Dancz. J. Chem. Phys. 70, 26 (1979).
10. Angular Momentum Constraints in Radiationless Processes: The Symmetric Top Molecule; With Frank A. Novak. J. Chem. Phys. (Submitted).
11. Low Energy Collisional Relaxation of 1_2^* in He: Evidence for Resonance Enhanced Vibrational Deactivation; With James Tusa and Mark Sulkes. J. Chem. Phys. 70, 3136 (1979).
12. Dynamics of Radiationless Processes Studied in Pulsed Supersonic Free Jets: Some Naphthalene Lifetimes; Chem. Phys. Letters 60, 364 (1979). With Fred M. Behlen and Nohiko Mikami.
13. Closing Remarks, Faraday Discussion #67. To be published in Discussions of the Faraday Society. Kinetics of State Selected Species. (In press).
14. Collision Induced Intramolecular Energy Transfer in Electronically Excited Polyatomic Molecules; Advances in Chemical Physics. Photoselective Chemistry Volume. Submitted August 1979.
15. Quantum Effects in Intramolecular Energy Transfer: The Role of Observations. With Ronnie Kosloff. Submitted to Chem. Phys. Letters.
16. The Influence of Rotational Motion on Intersystem Crossing in Isolated Molecules. With Frank A. Novak. Submitted to J. Chem. Phys.

We have conducted extensive studies of collisionally induced intramolecular vibrational relaxation in aniline. In the completed work Ar was the collision partner. The data show that the cross section for vibrational relaxation on the excited electronic surface is very large, that the pathway of vibrational relaxation is selective, and that endothermic processes are extremely important in the approach to equilibrium. This work has been augmented by studies of collision induced vibrational relaxation with water and methyl fluoride as partners and by a detailed study of the same processes in collisions between pyrazine and argon. These data are now being analyzed; we expect to submit manuscripts for publication within the next few months.

We have constructed a pulsed supersonic jet molecular beam apparatus to study the energy dependence of collision induced energy transfer. With this apparatus we have discovered a new, extremely efficient collision induced vibrational relaxation mechanism. We have thus far completed a study of collisions between helium, neon and argon atoms and electronically excited iodine molecules. We have found that extremely low relative kinetic energy collisions have essentially hard sphere cross sections for vibrational relaxation of the iodine molecule. A mechanism for this process based upon orbiting resonances has been proposed. Work now in progress includes extension of the study of very low energy collisions to the case of electronically excited polyatomic molecules and the development of a full quantum mechanical theory of the process.

We have extensively developed the theory of the effect of rotational state selection on radiationless processes, both molecule preserving and molecule destroying. We find, contrary to expectation,

that the role played by conservation of angular momentum so greatly constrains the possible final states that, in first order, initial selection of rotational state has no influence on the rate of the process. This is an important theoretical result, since it permits one to invert experimental observations and state with confidence that when a dependence of rate on initial rotational state is seen, there is a resonance interaction in the manifold of molecular states.

In addition to the work mentioned above, we have studied the behavior of large amplitude motion in molecules, shown the relationship between the onset of stochastic behavior and nonlinear resonances in a model molecule, probed the relationship between the onset of stochastic behavior and state-selective chemistry, and studied the representation of large amplitude motion in a molecule in terms of coherent states and solitary waves.

More detailed descriptions of all these studies can be found in the appended abstracts of the papers published (or submitted for publication).

Large Amplitude Vibrational Motion in a One Dimensional Chain: Coherent State Representation. With John Dancz
J. Chem. Phys. 67, 1418 (1977).

A study is made of the quantum mechanical motion of a one dimensional finite chain of anharmonic oscillators with free ends. It is shown that, for states which time evolve as coherent states (minimum uncertainty wave packets) of the normal mode vibrations, the motion is equivalent to a classical system with an effective potential interaction determined by convoluting the quantum wave packet and the potential energy. Some examples are discussed, with particular attention given to the Toda and Morse potentials, which are shown to be invariant in form under this convolution. The similarities between the classical Toda and Morse lattices are then utilized to infer the existence of compressional solitary waves in the Morse lattice from the well known soliton solutions of the Toda lattice. Further, for the Morse lattice an analytic expression is found for the first order perturbative correction to the Toda solitons for large amplitude vibrations. We also discuss the relation between the existence of such solitary waves and the rate of vibrational relaxation in molecular systems.

Spectroscopic Properties of Polyenes. III. 1, 3, 5, 7-Octatetraene.
With R. M. Gavin, Jr., Charles Weisman and Jeffrey K. McVey.
J. Chem. Phys. 68, 522 (1978)

Absorption and emission spectra of all-trans 1, 3, 5, 7-octatetraene are presented along with fluorescence quantum yields and lifetimes. In solution, a gap of about 3000 cm^{-1} is found between the first band of the $1^1A_g \rightarrow 1^1B_{\mu}$ transition and the onset of the emission spectrum. Excitation spectra of concentrated solutions at 77 K show low-lying bands in

this gap, the lowest energy band being almost coincident with the highest energy fluorescence band. On the other hand, gas phase fluorescence spectra show no gap between the lowest energy $1^1A_g \rightarrow 1^1B_\mu$ absorption band and the first fluorescence band. The radiative lifetime in hexane is 220 ns at room temperature and 190 ns at 77 K. The radiative lifetime for the gas phase fluorescence is estimated to be longer than 150 ns. The solvent dependence of the absorption and emission spectra, the fluorescence lifetimes, and the vibrational frequencies observed in solution imply support for the conjecture of Karplus et al. that the lowest excited singlet state is of 1^1A_g symmetry. The solution data imply that the low-lying state is about 6400 cm^{-1} below the 1^1B_μ level. On the other hand, the lack of a gap between absorption and emission and the long lifetime found for the gas phase are not compatible with this model.

On Vibrational Population Relaxation in Solution. With Joseph N. Kushick, Chem. Phys. Letters 52, 208 (1977).

A model is presented for the vibrational population relaxation of a polyatomic molecule in solution. The coupling of molecular vibrations leads to a cascade of energy through a sequence of vibrational levels. At each step of the energy redistribution energy can be transferred to nonvibrational (solvent) degrees of freedom. The model is developed in detail for a two step cascade, incorporating variable coupling potentials between zero order vibrational and solvent eigenstates. The results of these calculations are discussed in the context of time resolved picosecond laser studies of vibrational relaxation in liquids.

Internal Energy Transfer in Isolated Molecules: Ergodic and Nonergodic Behavior. In Proceedings of a Symposium on Advances in Laser Chemistry, California Institute of Technology, March, 1978. Ed. A. Zewail. Springer Verlag (1978).

This paper addresses the following questions:

1. Under what conditions, if any, is intramolecular energy exchange slow/rapid relative to other processes, for example photon emission, or isomerization, or fragmentation?
2. How does the intramolecular energy exchange depend on the energy of the molecule and the nature of the initial excitation?
3. If there are situations for which intramolecular energy exchange is slow relative to chemical reaction, why does this behavior occur? Does it derive from special characteristics of the molecular force fields? Are there dynamical or symmetry restrictions on the spectrum of states in these cases? Are these special situations commonly or rarely found?
4. Given the answers to (3), can we devise excitation methods and reaction conditions that permit enhancement of the selectivity of the chemistry that follows?

On the Influence of Nonrandom Sequential Coupling on Radiationless Relaxation Processes. With M. Muthukumar. J. Chem. Phys. 69, 1619 (1978).

We have considered radiationless decay in a simple skeleton spectrum of states between which there are systematic functional and random coupling matrix elements, the former are treated as a perturbation of the latter. As particular examples we have analyzed mixing of constant coupling and random coupling and mixing of Lorentzian coupling and random coupling in a spectrum which can model photodissociation and/or vibrational relaxation, and have calculated the total dissociation probability and

lifetime of the initially excited state. For small times the constant coupling-random coupling case leads to a linear combination of t and t^2 terms characteristic of nonsequential and sequential decays, respectively. The Lorentzian coupling-random coupling case can be thought of as a model for vibrational relaxation in solution. The calculated time evolution of the population of the initially excited vibrational mode exhibits two time constants for small times and is rather complex for larger times. The shorter time constant corresponds to the redistribution of energy among modes which are nearly resonant with the initially excited mode and the longer time constant corresponds to the relaxation to lower lying modes by the solvent. This is in good qualitative agreement with the experimental results of Kaiser et al.

On Rotational Effects in Radiationless Processes in Polyatomic Molecules. With Frank Novak and Karl Freed. In Radiationless Transitions, ed. S. H. Lin, (Academic Press, in press).

The theory of rotational effects in radiationless processes in polyatomic molecules is reviewed. Special attention is placed on effects of Coriolis coupling on internal conversion and intersystem crossing as introduced in the theory by Novak and Rice, and on the effects of rotational motion on product energy distribution in photodissociation as introduced in the theory by Morse, Freed, and Band.

Single Vibronic Level Fluorescence from Aniline. With Donald A. Chernoff. J. Chem. Phys. 70, 2511 (1979).

Gas phase fluorescence spectra of 15 vibronic levels in 1B_2 aniline are described. The emission spectra of single vibronic levels in aniline have well separated vibrational structure. A continuum background seen in a few cases is shown to be due to sequence congestion in the absorption spectrum, not to intramolecular vibrational energy transfer.

Collision Induced Intramolecular Vibrational Energy Transfer
in 1B_2 Aniline. With Donald A. Chernoff. J. Chem. Phys. 70,
2521 (1979).

The technique of SVL fluorescence spectroscopy was used to observe collision-induced intramolecular energy transfer in a large polyatomic molecule in the gas phase. Vibrational energy transfer was traced from eight vibronic levels in 1B_2 aniline with argon as a collision partner. Overall rates for depletion of the initial level range from 0.1 to 0.5 of the equivalent hard sphere collision rate. The vibrational levels below 800 cm^{-1} are found to fall into groups; energy transfer is much more efficient between levels in the same group than between levels in different groups. This pattern of energy disposal indicates that specific dynamic characteristics of the vibrational modes are as important as the energy gap and vibrational overlap integrals. Another interesting feature of the results is the importance of endoergic processes, even when exoergic pathways for vibrational energy exchange are available. Rotational relaxation was also examined, but only with low resolution, and not in a systematic study. The rate of rotational equilibration found approximates the collision rate.

A Numerical Study of Large Amplitude Motion on a Chain of Coupled Nonlinear Oscillators. With Timothy J. Rolfe and John Dancz. J. Chem. Phys. 70, 26 (1979).

We have studied the behavior of large amplitude compressive displacements on one-dimensional lattices of equal masses which interact with a variety of nearest neighbor potential energy functions. For the cases of cyclic and fixed end boundary conditions solitons are found to exist and to completely determine the dynamics. The shapes of the solitons on the several lattices are remarkably alike, and all are very close to the shape of a Toda lattice soliton. Because reflection at a free end creates

a dilational displacement, a solitary wave does not survive on a lattice with free ends. Mass inhomogeneities in the lattice also scatter solitary waves and lead to their destruction, but the rate of the process depends on the defect to host mass ratio. When that mass ratio is 13/12 a solitary wave survives at least 500 collisions, and its energy is modulated cyclically. The rate of destruction increases as the defect to host mass ratio increases. The results of the calculations are discussed with respect to the ubiquity of solitary wave behavior, its relation with the shape of the potential energy curve, and the possible role of metastable solitary pulses in intramolecular energy transfer.

Angular Momentum Constraints in Radiationless Processes: The Symmetric Top Molecule. With Frank A. Novak. J. Chem. Phys. (In press).

The effects of rotational motion on the rate of intramolecular radiationless relaxation in polyatomic molecules is investigated in symmetric tops. The molecule is assumed to have the same symmetry in both the initial and final states so that vibration and rotational degrees of freedom remain separated during the relaxation. The effect of intermanifold Coriolis interaction on an internal conversion process between two singlet states is discussed in detail. The effect of Coriolis interaction on the intersystem crossing rate is also formulated, however, a detailed calculation is not performed.

Low Energy Collisional Relaxation of I_2^* in He: Evidence for Resonance Enhanced Vibrational Deactivation. With James Tusa and Mark Sulkes. J. Chem. Phys. 70, 3136 (1979).

Experimental studies of collisional relaxation of excited iodine molecules reveal a large vibrational depopulation cross section for the case of collisions with very small relative kinetic energy. The observations are interpreted in terms of orbiting resonances of the collision pair.

Dynamics of Radiationless Processes Studied in Pulsed Supersonic Free Jets: Some Naphthalene Lifetimes. With Fred M. Behlen, and Naohiko Mikami. Chem. Phys. Letters 60, 564 (1979).

A pulsed supersonic free jet is used to prepare a low temperature sample of naphthalene vapor. Single vibronic level fluorescence lifetimes determined therein differ significantly from lifetimes previously obtained at room temperature.

Closing Remarks, Faraday Discussion #67. To be published in Discussions of the Faraday Society. Kinetics of State Selected Species. (In press).

These remarks present an overview of the topics considered at the Faraday Society Discussion on kinetics of state selected species. Attention is called to areas where more information is needed.

Collision Induced Intramolecular Energy Transfer in Electronically Excited Polyatomic Molecules. Advances in Chemical Physics. Photoselective Chemistry Volume. Submitted August 1979.

This article surveys the theoretical and experimental information available concerning collision induced intramolecular energy transfer in electronically excited polyatomic molecules. Attention is focused on the existence of propensity rules for intramolecular vibrational energy transfer and on the importance of up-pumping in a collision.